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BROWNIAN MIGRATION OF CRYSTALLITES ON A SURFACE
The case of aluminum on KCl. Clarification of the slip mechanism. Part III.

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BROWNIAN MIGRATION OF CRYSTALLITES ON A SURFACE.

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ABSTRACT.

It is shown experimentally that crystallites of aluminum are able to migrate on a (100) KCl substrate (contact plane (111)). The measurements give a free activation enthalpy of their diffusion which contains a term ΔG_o which is independent of the crystallites dimensions and a term ΔG_m proportional to the contact area of the crystallites. ΔG_m becomes zero at a temperature $T = 465^oK$. The interface model of the crystallites given in paper (II) gives to T_o the meaning of the "melting"temperature of the islands which ensure the coherence between deposit and substrate. ΔG_m is the free enthalpy of "melting" of these islands, ΔG_o is the activation free enthalpy of the interface viscosity if there is no coherence.

I - INTRODUCTION

In two preceeding articles, I and II[1,2], we established the experimental fact that crystallites of gold deposited by thermal vaporization on the (110) KCl cleavage were so animated by a translational and rotational motion that their epitaxial order with the surface was not obtained. A theoretical study of the interface between the crystallite and the substrate gave an idea of the crystallite slip mechanism.

The goal of this work is to show that the observed phenomenon exists in systems other than Au/KCl. The system of aluminum on (100) KCl was chosen because the crystallite of aluminum rarely presents (111) twinning whereas gold crystallites are complicated multi-twinned buildings. One knows that the stacking fault energy is on the order of 200 ergs cm^{-2} for Al where as it is only 55 ergs cm^{-2} for Au. However, Al as Au are face centered cubic metals with very similar parameters (4.0784 and 4.0787 Å respectively). The comparison of the two systems will help clarify if the migration phenomenon of Au is attributable to the complexity of the gold crystallite structure. From this study, we strove to achieve better experimental measurements inorder to be able to deepen the understanding of the interface model and the slip mechanism of crystals.

II - EXPERIMENTAL TECHNIQUE

The principle that we used to measure the migration of grains of Al on (100) KCl is the same as the one previously used[1], i.e., a crystallite distribution is realized on a partial area of a (100) contact plane of KCl. In practice, the clear boundary between the zones with and without the grains was obtained. It was obtained by masking a small area of the cold cleavage (100) KCl surface during the grain deposit with the edge of a lamina. Here, we use a different technique that is easier and more efficacious, that we tested first on the Au/KCl[4] system[1].

Inorder to produce the partial area plane occupied by the aluminum grains on (100) KCl, one takes advantage of the shadow carried by the raised step of the surface by the incident jet of metallic vapor making a specific angle with the surface of the substrate. The sequence of the experiment follows: in a high vaccuum chamber where a pressure of $5 \cdot 10^{-9}$ Torr is never exceeded, we cleave a crystal of KCl at a temperature of 20°C. Immediately after an obturator releases for a determined time an aluminum jet (10^{14} at cm^{-2} sec^{-1}) whose angle of incidence with respect to the normal to the surface is 30° (fig. 1a). The aluminum vaporization is carried out by a near pin-point source (Knudsen cell for aluminum) inorder to better resolve the penumbra effect (for a step height of 1μ, a cell effusion opening of $3 \cdot 10^{-12}$ cm placed 12 cm from the cleavage surface gives a penumbra of 30 Å). An annealing is then carried out at the temperature T for a time t at the end of which the cleavage surface is covered with a carbon film that is 200 Å

thick which fixes the grains and allows thier extraction for microscopic and electronic diffraction observation.

On figure 1b, of the electronic micrograph, we observe the development of the ensemble on the cleavage surface. The raised step which interests us is recognizable by a succession of zones represented by the variations in thickness, thus transmission of the carbon replica.

- Zone A which is the thinnest and thus clearest, corresponds to the abrupt slope of the step. It is surrounded by two zones B and C.

- In zone B the grain distribution comes up to the limit between A and B. According to the figure 1a, one knows that it corresponds to the height of the step.

- Zone C, the lower section of the step, consists of two regions of which the frontier will be examined. The one free of crystallites corresponds to the shadow of the step, the other carries a grain distribution.

We have thus achieved a series of independent experiments, production of a clear boundary at 20°C and development of this limit by an annealing at a temperature T for a time t.

The analysis of the electronic micrographs consists of tracing in a perpendicular direction to the limits of the grains a density curve from the two dimensional distribution of the crystallites on the surface. The principle of the analysis is the same as the one described in a previous article[1]. Figure 2a represents the standardized concentration profile of the document (fig. 1b) obtained according to the following treatment: T = 140°C, t = 2 minutes.

We have used in this study a much more precise technique since we were able to calculate in advance the dimensions of the crystallites with the help of a CARL-ZEISS TGZ3 particle dimension analyser (the error of the sieve grading in measuring the dimensions of the crystallites for an enlargement of 400,000 is around 2 Å).

III - EXPERIMENTAL RESULTS

We have plotted the diffusion profiles of the aluminum grains on (100) KCl for different gradings of diameter d = 14, 18, 22, and 26 Å.

- The annealing temperatures reached from T = 20°C to 190°C, an interval during which the grading remains the same. In this range, the morphology and the electronic diffraction patterns show that the crystallites of aluminum are not twinned; they are resting on the (111) contact plane and are found azimuthally disoriented on the (100) KCl substrate.

- The diffusion profiles of the grains of different dimensions possess the same inflection point.

- Figure 2 gives two standardized profiles of the grain concentration of diameters d = 26 and 14 Å with an annealing temperature of T = 140°C and 180°C respectively, t = 2 minutes. This constitutes the proof of the aleatory movement of the aluminum crystallites (see[1]).

- In the range of T = 160 to 190°C, the diffusion coefficients D_c of the grains are easily measurable. (Beyond 190°C, a grain coalescence begins, a phenomonen that we won't study here.) The

results of the experiments are presented in figure 3 giving the diffusion coefficients D_c ($cm^2 sec^{-1}$) as a function of the diameter d of the crystallites.

Figures 3a, b, c, and d, correspond to four annealing temperatures T; the lines were drawn by the method of least squares in the functional scale $(\log D_c) - d^2$.

IV - SLIP MECHANISM OF THE GRAINS AND THE STRUCTURE OF THE INTERFACE.

In a previous article[2], we have shown that the aleatory movements of the crystallites on a substrate, whose interface has a certain viscosity opposing the displacements, permitted the definition of a crystallite diffusion coefficient:

$$1) \qquad D_c = 2a^2 \frac{kT}{h} \exp\left(-\Delta G_v^*/kT\right)$$

with ΔG_v^* the free activation enthalpy of the slip for a distance a, h and k, Planck's and Boltzmann's constants.

We have presented[2] an interface model of a metal crystallite c.f.c. with a contact plane (111) on (100) KCl. Such an interface presents islands of atoms adhering to each other and to the interface. They are distributed in a periodic manner (fig. 4) and are surrounded in a disordered arrangement as in a liquid. We will clarify the slip mechanism of the crystallites here.

The slip of a crystallite requires a loss of coherence with the substrate, i.e., the "melting" of the coherent islands. The slip accomplished, the islands reappear as before.

1) The first stage preceeding the crystallite translation, the disappearance of the coherent islands, can be identified as a transformation of the first order with ΔH_m and ΔS_m the latent enthalpy and entropy, such that at a temperature T_o ("melting" temperature of the islands), the free enthalpy of transformation ΔG_m becomes zero, being in first approximation[2])

$$2) \quad \Delta G_m = \Delta H_m \ (1 - T/T_o)$$

Since the number of coherent atoms contained in all the islands of the interface is proportional to the contact area of the cristallites with the substrate, then the relation (2) can be written:

$$3) \quad \Delta G_m = \frac{\pi d^2}{4a^2} \ \Delta h_m \ (1 - T/T_o)$$

if d is the diameter of the grains supposed hemispherical, a^2 the area of the atom, Δh_m the latent transformation enthalpy ascribed to an atom of the interface.

2) The coherent islands gone, the interface has a disordered structure and the slip of the crystallite takes place on a viscous bed. By treating the viscosity (according to Eyring[5]) as if caused by mobile holes in the material and the slip of the two adjacent planes as if caused by the movement of a hole from one equilibrium position to the next, one can identify the free activation enthalpy of the slip as that of the formation and migration of a hole:

$$4) \quad \Delta G_o = \Delta H_o - T\Delta S_o$$

The slip of a cristallite is achieved when the barriers (3) and (4) are surmounted, in other words:

$$5) \quad \Delta G_v^* = \Delta G_m + \Delta G_o$$

Expression (1), from (5), (4), (3) gives the diffusion coefficient of a crystallite:

$$6) \quad D_c = 2a^2 \frac{kT}{h} \exp(\Delta S_o/R) \exp(-\Delta H_o/RT) \exp \frac{\pi d^2 \Delta h_m}{4a^2 R} (1/T - 1/T_o).$$

V - DISCUSSION

We will compare the relation (6) with the experimental data of figure 3. The experimental points obtained for the four temperatures T = 160, 170, 180, 190°C correspond to the relation:

$$7) \quad \log D_c = A + B \cdot d^2$$

according to (6):

$$7') \quad B = \frac{\pi \Delta h_m}{4a^2 R} \quad (1/T - 1/T_o)$$

$$7'') \quad A = \log 2 a^2 \frac{kT}{h} + \frac{\Delta S_o}{2.3R} - \frac{\Delta H_o}{2.3RT}$$

The slopes B of the lines of figure 3 given as a function of 1/T (fig. 5) give:

$$T_o = 465^\circ K \text{ and } h_m = 0.5 \text{ kcal}$$

(fixing a = 2Å).

The ordinate at the origin A of figure 3 given as a function of 1/T (fig. 6) lead to

$$H_o = 15 \text{ kcal and } S_o = -14 \text{ cal deg}^{-1}$$

One can discuss the significance of the numerical values thus found.

- $T_o = 465^oK$ would be the "melting" temperature of the coherent islands on the interface. According to the interface model[2] of (111) Au - KCl (100), geometrically applicable to (111) Al - KCl (100), the number of atoms in the islands represents one fifth of the total number of atoms in the interface. For each atom of an island the latent "melting" enthalpy was thus $5\Delta h_m = 2.5$ kcal, a value that is on the same order of magnitude as the transition energy of the first order between the condensed phases.

- The values ΔH_o and ΔS_o would represent the enthalpy and the entropy of formation and migration of the holes in the interface when it is disordered. These magnitudes determine the dynamic friction coefficient of the crystallites on the substrate beyond the temperature T_o as it was defined in the previous article[2]:

$$8) \qquad \mu = h/a^2 \; e^{-\Delta S_o/R} \; e^{\Delta H_o/RT}$$

being the bidimensional viscosity connected to the tridimensional viscosity η by

$$9) \qquad \eta = \mu/a$$

For $T_o = 465^oK$ and the numerical values of ΔH_o and ΔS_o determined experimentally ($a = 2\text{Å}$), then $\eta_o \simeq 10^7$ poises. We will note that the viscosities of the liquids in the neighborhood of the melting point rise several 10^{-2} poises, where as those of the solids at the point of melting rise several 10^{20} poises. The crystallite interface is thus the intermediate position between the two states; this supports in our interface model the hypothesis of a disordered layer.

For $T < T_o$, there exist anchoring points (coherent islands), the viscosity of the interface becomes a function of the area of contact of the cristallites, being:

$$10) \qquad \eta = h/a^3 \; a^{\Delta G_o/RT} \; e^{\Delta G_m/RT}$$

with ΔG_o and ΔG_m given respectively by (4) and (3). Thus, for a crystallite of 20 Å in diameter at $T = 273^oK$, one will have, according to (10) and the determined experimental values, $\eta \simeq 10^{24}$ poises, a value which approaches the viscosity of a solid. The interface thus presented is rigid.

In this article we have been able to clarify the mechanism of rownian migration of small cristallites on a surface. In addition, the experiments made on the Al/KCl system confirm those already published on Au/KCl; this has led us to believe that the phenomenon studied can be generalized.

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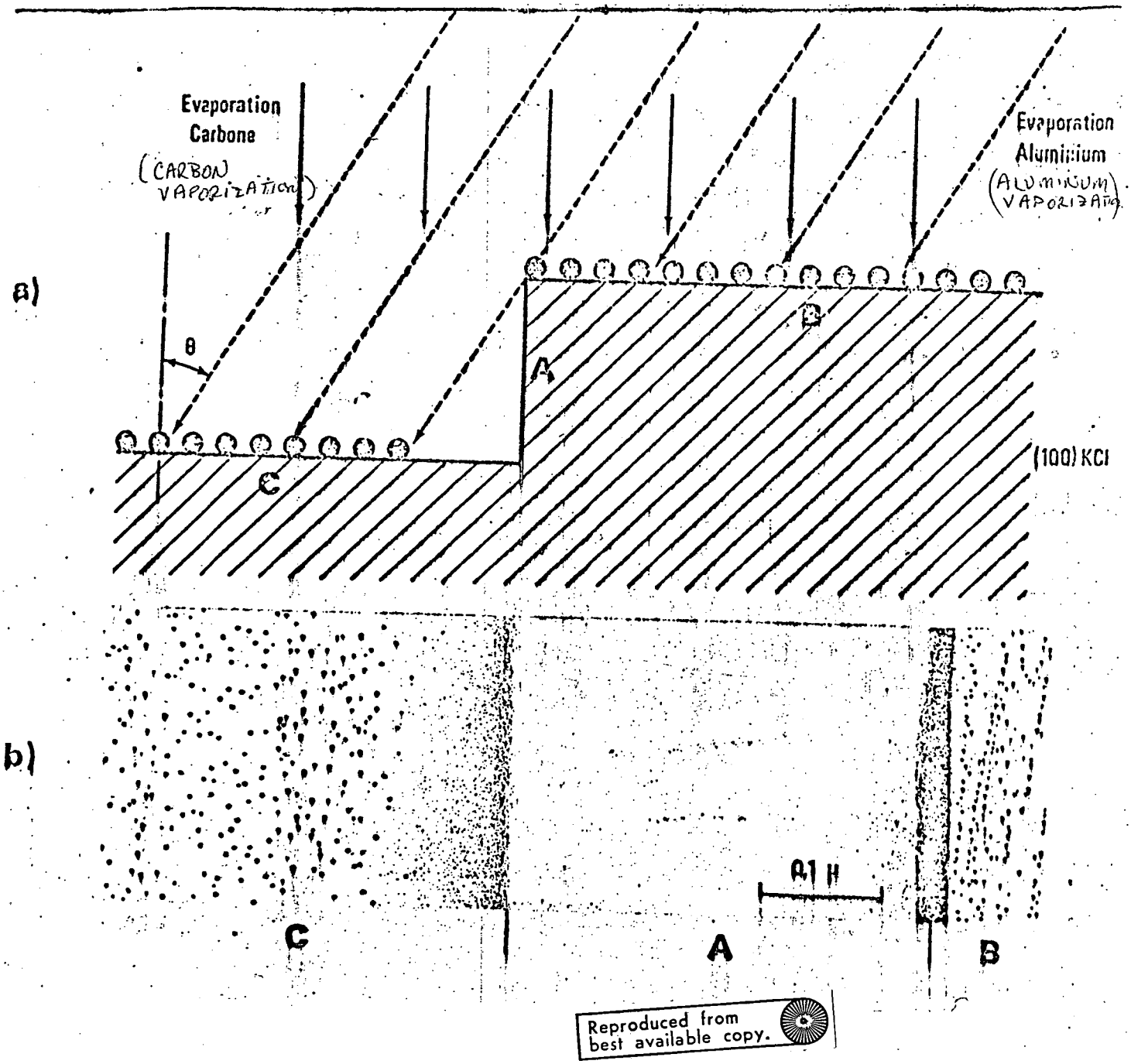

Figure 1. Shadow method of high steps

a) schematic of the experimental principle

b) corresponding micrograph for an annealing

T = 140°C, t = 2'.

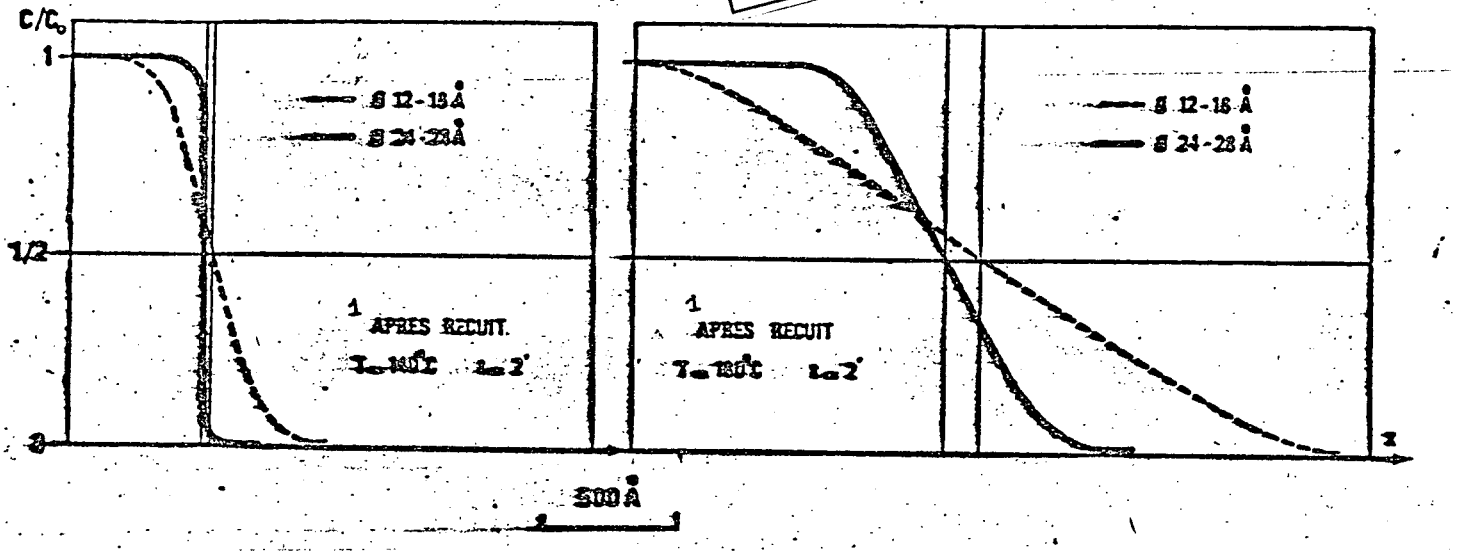

Figure 2. Bidimensional Al Crystallite Distribution for two gradings, d = 26 and 14 Å

a) annealing T = 140°C, t = 2'

b) Annealing T = 180°C, t = 2'

Key 1 - after annealing

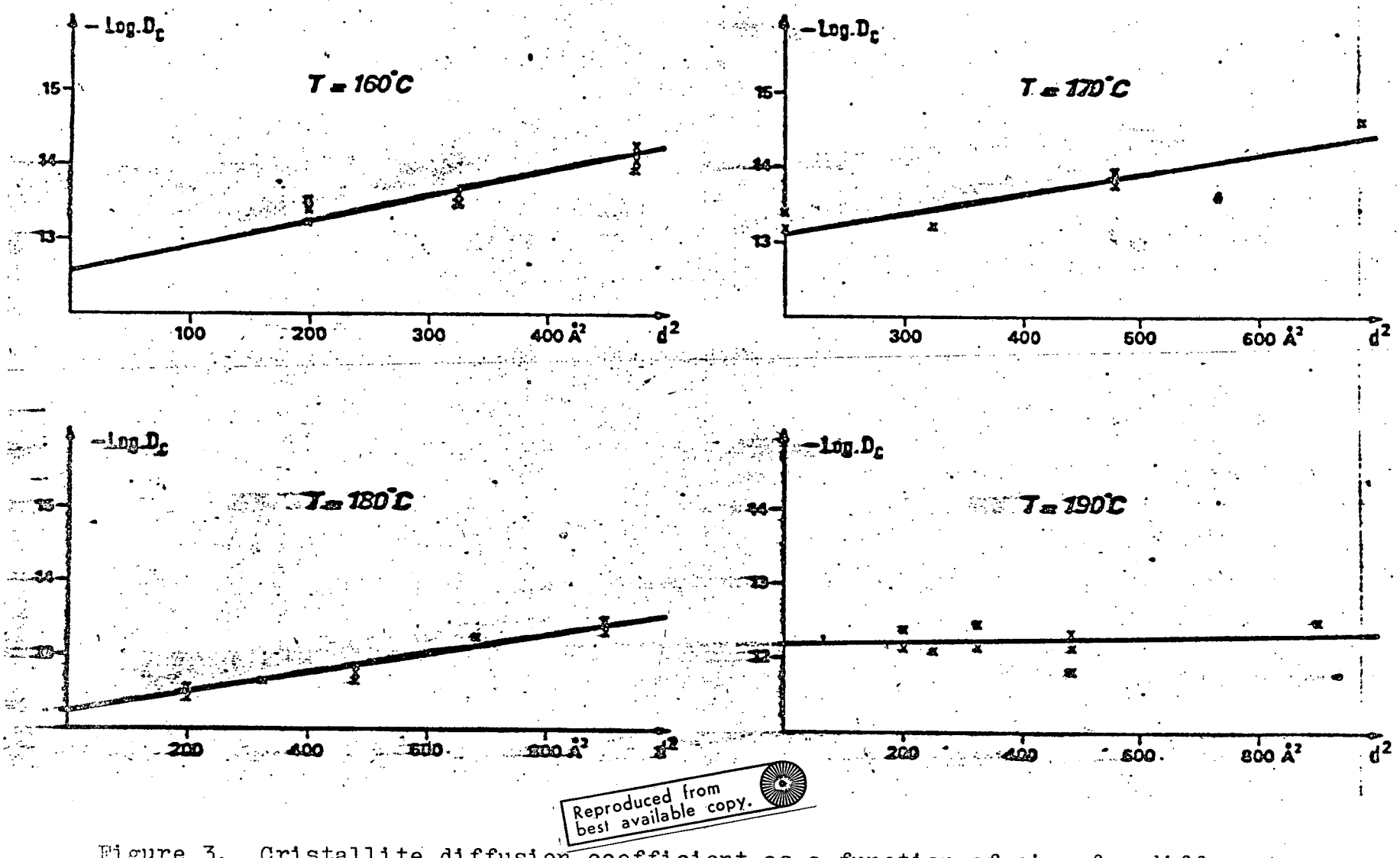

Figure 3. Cristallite diffusion coefficient as a function of size for different temperatures: T = 160, 170, 180, and 190°C.

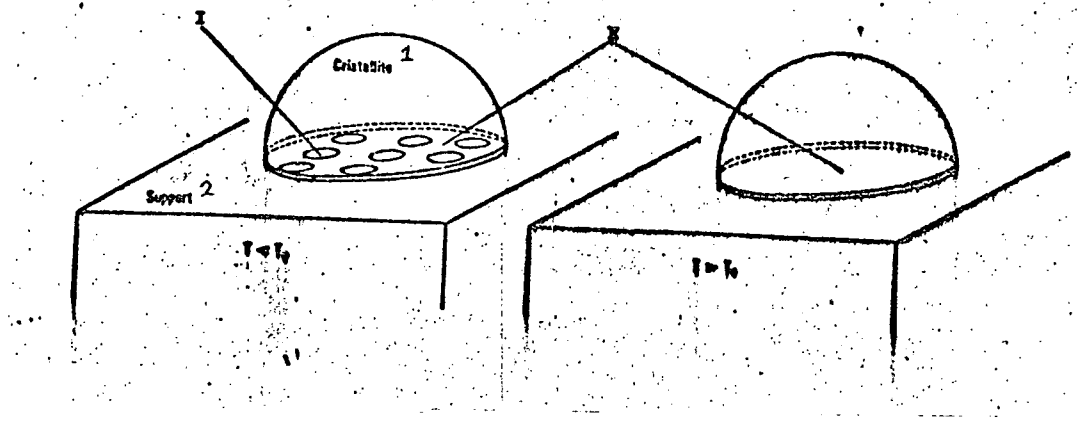

Figure 4. Schematic of crystallite interface largely disoriented on the substrate for T T_0 and T T_0, I. coherent island II. disordered island.

key 1 - substrate

2 - crystallite

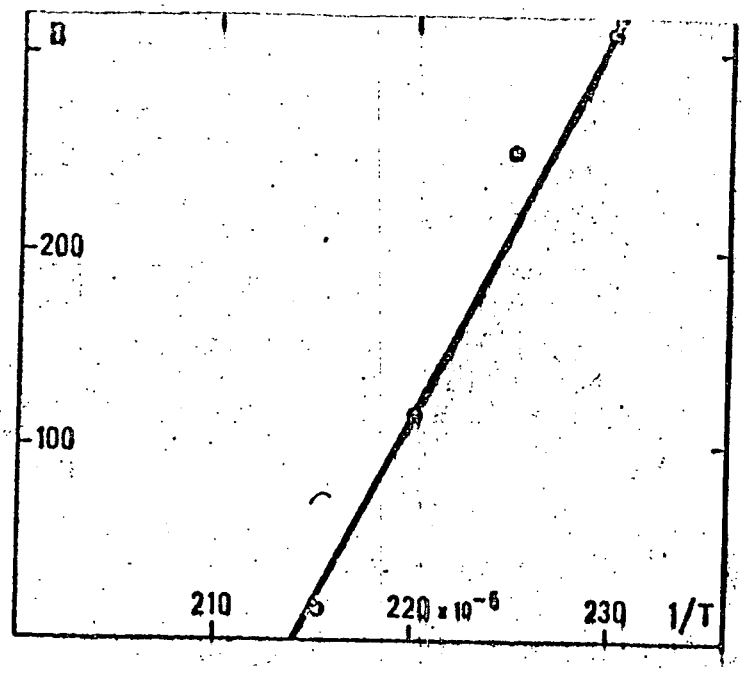

Figure 5. Slope B of the curves of figure 3 as a function of 1/T.

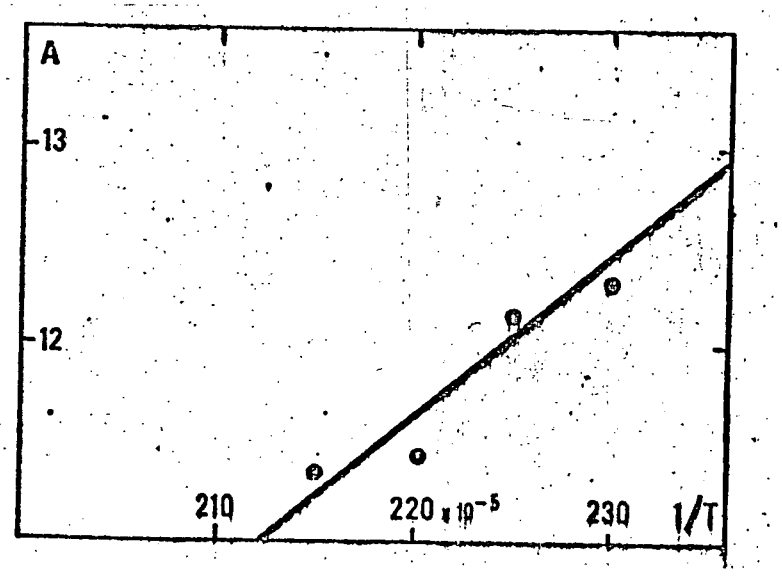

Figure 6. Ordinates form the origin A of figure 3 as a function of 1/T.

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